XP-002155642

AN - 1986-128289 [25]

AP - JP19840187067 19840906; JP19840187067 19840906

CPY - TAIO

DC - L03 M13 U11 X12

FS - CPI;EPI

IC - C09D5/24; H01B1/16; H05K1/09; H05K3/12

MC - L03-A01A3 L03-H04E4 M13-B

- U11-A05 X12-D01X

PA - (TAIO) TAIYO YUDEN KK

PN - JP61066303 A 19860405 DW198620 005pp

- JP3012789B B 19910221 DW199112 000pp

PR - JP19840187067 19840906

XA - C1986-054860

XIC - C09D-005/24; H01B-001/16; H05K-001/09; H05K-003/12

XP - N1986-094723

AB - J61066303 Paste is composed of 49-91 wt% Ag, Pd, Au, Pt noble metal powder and 6-20 wt% glass frit and 3-31 wt% at least 1 kind of Zn, Al, Sn, which are bonded by binder.

 ADVANTAGE - Electroconductive paste is directly printed on surface of conductor, surface is not oxidised in baking process in air and

appropriate conductivity is obtd.

- In an example, Ag powder 12 g+Zn powder 5 g+CaO-BaO-SiO2 glass frit 19 g+ethylcellulose binder 6 g+alpha-terpineol 33 g were kneaded in 3 roller mill to give electro-conductive paste. In conventional method for preventing oxidn. base metal part was Ni-plated and then noble metal was plated on the Ni-plated part, so that process was complicated and cost was raised up. Even when sample was baked in oxidising atmos. electric resistance was stable (not increased). Tensile strength was also stable.

IW - THICK LAYER ELECTROCONDUCTING PASTE COMPOSE SILVER PALLADIUM GOLD PLATINUM GLASS FRIT ZINC BOND BIND

IKW - THICK LAYER ELECTROCONDUCTING PASTE COMPOSE SILVER PALLADIUM GOLD PLATINUM GLASS FRIT ZINC BOND BIND

NC - 001

OPD - 1984-09-06

ORD - 1986-04-05

PAW - (TAIO) TAIYO YUDEN KK

TI - Thick-layer electroconductive paste - composed of silver, palladium, gold, platinum, glass frit and e.g. zinc bonded by binder



GROUP 1700

MACHINE-ASSISTED TRANSLATION (MAT):

(19)【発行国】 日本国特許庁(JP) (19)[ISSUING COUNTRY]

Japanese Patent Office (JP)

(12)【公報種別】 公開特許公報(A)

Laid-open (kokai) patent application number (A)

(11)【公開番号】 昭 61-66303

(11) [UNEXAMINED PATENT NUMBER]

Showa 61-66303

(51)【国際特許分類第4版】 H01B 1/16

C09D 5/24 H05K 1/09

(51)[The 4th edition of International Patent

Classification1' H01B 1/16 C09D 5/24 H05K 1/09

【職別記号】

[Identification symbol]

【庁内整理番号】

8222-5E 6516-4J 6679-5F

[An internal arrangement number]

8222-5E 6516-4J 6679-5F

(43)【公開日】

昭和61年(1986)4月5日

(43)[DATE OF FIRST PUBLICATION]

April 5th, Showa 61 (1986)

【審査請求】

未請求

[EXAMINATION REQUEST]

UNREQUESTED

【発明の数】

[NUMBER OF INVENTIONS] One

【全頁数】 5 [NUMBER OF PAGES] Five

(54)【発明の名称】

厚膜用導電ペースト

(54)[TITLE]

The electroconductive paste for thick films

(21)【出願番号】 昭 59-187067

(21)[APPLICATION NUMBER] Showa 59-187067

(22)【出願日】

(22)[DATE OF FILING]

00/10/30

1/12

(C) DERWENT

JP61-066303

DERWENT

THOMSON SCIENTIFIC

昭 59(1984)9 月 6 日

Showa 59 (1984) September 6th

(72)【発明者】

(72)[INVENTOR]

【氏名】 登坂 正一

Shoichi Tosaka

【住所又は居所】

[ADDRESS]

東京都台東区上野1丁目2番12号 太陽誘電株式会社内

(72)【発明者】

(72)[INVENTOR]

【氏名】 広岡 晋

Shin Hirooka

【住所又は居所】

[ADDRESS]

東京都台東区上野1丁目2番12 县 大陽縣電井十分社内

号 太陽誘電株式会社内

(71)【出願人】

(71)[PATENTEE/ASSIGNEE]

【氏名又は名称】

太陽誘電株式会社

Taiyo Yuden Co., Ltd. K.K.

【住所又は居所】

[ADDRESS]

東京都台東区上野1丁目2番12

号

(74)【代理人】

(74)[PATENT AGENT]

【弁理士】

[PATENT ATTORNEY]

【氏名又は名称】

北條 和由

Kazuyoshi Hojo

【明細書】

[SPECIFICATION]

【1.発明の名称】

厚膜用導電ペースト

[1. TITLE]

The electroconductive paste for thick films

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2/12

(C) DERWENT

【2.特許請求の範囲】

Ag,Pd,Au,Pt 等の貴金属粉末が49~91 重量%と,ガラスフリットが6~20 重量%と,Zn,Al,Sn の1 種以上からなる粉末が3~31 重量%とからなるものをバイダーで粘結させてなることを特徴とする厚膜用導電ペースト。

【3.発明の詳細な説明】

【産業上の利用分野】

この発明は、いわゆるスクリーン印刷法等の厚膜法により、混成集積回路等を製造するのに使用される導電ペーストに関する。

【従来の技術】

導電ペーストを空気中で焼成する場合,金属増化を原を変して、 を空気の酸化にくれる。 を関係した。 をののののので、 のののので、 ののののので、 ののののので、 ののののので、 ののののので、 のののので、 ののので、 ののので、 ののので、 ののので、 ののので、 ののので、 ののので、 ののので、 ののので、 のので、 の

しかし、上記基板の上に被膜抵

[2. Claim]

That which consists of noble metal powders, such as Ag, Pd, Au, and Pt, of 49 - 91 weight%. glass frit of 6.- 20 weight%, and powder which consists of 1 or more sorts of Zn, Al, and Sn of 3 - 31 weight%, is made to cake with a binder.

The electroconductive paste for thick films characterized by making as above-mentioned.

[3. DETAILED DESCRIPTION OF INVENTION]

[INDUSTRIAL APPLICATION]

This invention relates to the electroconductive paste used for producing a hybrid integrated circuit etc. by thick film methods, such as the so-called screen printing method.

[PRIOR ART]

When circuit apparatuses, such as a hybrid integrated circuit; are generally produced by the thick film method, the method in which while according to a predetermined wiring pattern, an electroconductive paste is printed by the screen printing method, using the ceramic substrate which has a through-hole as a base, the above through-hole is filled with said paste, and these are printed is adopted.

When baking an electroconductive paste in air, in order to prevent the gain of the resistance value by the oxidation of a metal component, the electroconductive paste which essentially consists of noble metals, such as Ag, Au, and Pt, is used. However, these are expensive.

Then the method of using the electroconductive paste which essentially consists of base metal, such as Ni, and baking this in inert gases, such as N2 gas, as an object for inexpensive, is utilised.

However, baking in air the resistive paste which essentially consists of RuO2 used in order to compose a film resistor on an above substrate is needed.

For this reason, when a film resistance is

抗体を構成するのに使用されて いる RuO2 を主成分とする抵抗 ペーストは,空気中で焼成する ことが必要とされている。この ため,被膜抵抗を構成するとき は,卑金属を主成分とした導電 ペーストを焼成した後,酸化防 止のため,外部に露出した卑金 属導体を貴金属でメッキした 後,この上から貴金属を主成分 とする導電ペーストや上記抵抗 ペーストを印刷し,これを空気 中で焼き付けるという方法が採 られていた。

composed. after baking processing electroconductive paste which essentially consists of base metal, the base metal conductor exposed externally was galvanized with noble metals for anti-oxidation. Then, the electroconductive paste and the above resistive paste which essentially consists of noble metals are printed from on this. The method of printing this in air was taken.

【発明が解決しようとする問題 [PROBLEM ADDRESSED] 点】

しかし,貴金属メッキによる酸 化防止処理に際しては.まずセ ラミック基板の表面に露出して いる卑金属導体のみに Ni メッ キを施した後,その上を貴金属 られる。従って比較的複雑な工 程が必要となり,これが卑金属 ペーストを使用することによっ て得られるコスト低減効果を大 幅に減殺する結果となる。

この発明は,上記の従来の問題 を解消すべくなされたものであ って,貴金属とガラスフリット からなる導電ペーストに少量の Zn,Al またはSn を加えることに より,これを卑金属導体の表面 に塗布して焼成した際に、同卑 金属導体の界面で酸化を防止す る作用があることに着目し,費 金属メッキ等,特別な酸化防止 処理をせずに直接導電ペースト を印刷して,これを空気中で焼 成できるようにしたものであ る。

However, in the anti-oxidation process by noble metals plating, the procedure which carries out plating of the it top with noble metals first after giving Ni plating only to the base metal conductor exposed to the surface of a ceramic substrate is taken.

Accordingly a relatively complicated process でメッキするといった手順が採 is needed. This is why the cost reduction effect obtained by using a base metal paste is eliminated sharply.

> This invention is made that the abovementioned conventional problem should be eliminated. It paid attention that there is an effect which prevents an oxidation by the boundary surface of said base metal conductor when applying a coating and baking processing this on the surface of a base metal conductor, by adding a small amount of Zn, Al or Sn to noble metals and the electroconductive paste which consists of the glass frit. A direct electroconductive paste is printed, without carrying out a special anti-oxidation process. such as noble metals plating etc. It enables it to bake this in air.

【問題を解決するための手段】 この発明による厚膜用導電ペーストは,Ag,Pd,Au,Pt 等の貴金属 粉末が 49~91 重量%と,ガラスフリットが 6~20 重量% と,Zn,Al,Snの1種以上からなる 粉末が 3~31 重量%とからなる ものである。

ガラスフリットには,CaO-BaO-SiO2 系ガラス等の硼珪酸ガラスが一般に使用される。

【作用】

なお,導電ペーストの組成比を上記のように限定した理由は,

[Means for solving a problem]

The electroconductive paste for thick films by this invention, consists of noble metal powders, such as Ag, Pd, Au, and Pt, of 49 - 91 weight%, glass frit of 6 - 20 weight%, and the powder which consists of 1 or more sorts of Zn, Al, and Sn is 3 - 31 weight%.

Borosilicate glasses, such as CaO-BaO-SiO2-based glass, are generally used for the glass frit.

[EFFECT]

When the electroconductive paste by this invention is used, noble metals plating is not made to the surface of the base metal conductor baked in the inert gas, but said paste is directly printed in piles on this. This is baked in air.

Then, the conduction state required for electric connection of a circuit is obtained at the contact of a base metal conductor and the conductor which bakes an above electroconductive paste and was obtained).

This is considered to be caused the reason below.

If an above electroconductive paste is baked in air, metals, such as Zn, Al, Sn, etc. which exist near the boundary surface with a base metal conductor, will take oxygen from said base metal conductor, and will oxidize. In the glass component by which the sintering was carried out, this is received and makes and disperses.

metal conductor, metal components, such as Ni in it, will be, so to speak, in the reduction state. This is not oxidized, but reacts with the noble metals components in an above electroconductive paste, such as Ag, Pd, Au, and Pt, and an electric conduction state is formed.

In addition, the reason which limited the composition ratio of an electroconductive paste as mentioned above is as following.

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次ぎの通りである。

(2)ガラス成分が少な過ぎると 導体間の接着強度が低くなり、 逆に多過ぎると焼結されたガラ ス成分が導体間の接合面を覆い、導体間の接触抵抗が高くな る。この点から 6~20 重量%の 組成比が必要である。

【実施例】

次ぎにこの発明の実施例を説明する。 Ag 粉末 63g,Pd 粉末 12g,Zn 粉末 6g 及び CaO-BaO-SiO2 系ガラスフリット 19g に バインダーとしてエチルセルローズ 6g と α -ターピネオール 33g を加え、3 段式ロールミルで 混練し、別表の試料番号 55 で示された組成を有する導電ペーストを作った。

さらにこの他にも同様の方法で,別表の試料番号3~5,7~9,13~17,21,22,24~26,29~33,36~39,43~45,49,50,52,54~61,64~71,73~77,79~85で示された組成を有する導電ペースト

(1) If there are many metal powders, such as Zn, Al, and Sn, the quantity of the oxide produced when baking processing an electroconductive paste in air will increase. As a result of said oxide's dispersing so much in a glass component, there is trend that the adhesion strength of a conductor reduces.

Moreover, the above oxide which exists in a noble metals grain boundary, without dispersing in glass raises the resistance value of a conductor.

These need to be 31 weight% or less practically from this point.

Moreover the composition ratio requires 3weight% in the minimum in order to do an above effect so.

(2) If a glass component is too few, the adhesion strength between conductors will become low. Conversely if it is too much, the glass component by which the sintering was carried out will wear the connection surface between conductors, and the contact resistance between conductors will become high.

The 6 - 20-weight% composition ratio is required from this point.

[Example]

The Example of this invention is explained below.

Ethyl cellulose 6g and (alpha)- terpineol 33g is added as a binder to 63g of Ag powder, 12g of Pd powder, 6g of Zn powder and CaO-BaO-SiO2-based glass frit 19g. Kneading is carried out by the 3 step formula roll mill. The electroconductive paste which has the composition shown by the sample number 55 of the attached table was made.

Furthermore in addition to this, the electroconductive paste which has the composition shown by the sample number 3 - 5 of the attached table, 7 - 9, 13 - 17, 21 and 22, 24 - 26, 29 - 33, 36 - 39, 43 - 45, 49, 50 and 52, 54 - 61, 64 - 71, 73 - 77, and 79 - 85 was respectively made by the similar method.

をそれぞれ作った。

【使用例及び試験例】

次ぎに.上記実施例で得られた 導電ペーストを次ぎのような方 法で使用し,かつ試験を実施し た。

複数の貫通孔を有する厚さ 200 μ m の未焼結磁器シートに, 所定の配線パターンに従っ て,Ni を主成分とする導電ペー ストをスクリーン印刷すると共 に,貫通孔に上記導電ペースト を充填した。次いで,この未焼結 磁器シートを 125℃の温度で 10 分間加熱して乾燥した後.所定 の順序で 4 枚積層して圧着し た。次いでこれを 900℃の温度 で熱処理して磁器シート及び導 電ペースト中のバインダ成分を 除去した後,2%の H2 を含む N2 ガス雰囲気中で 1200℃の温度 下に 2 時間置き、図面に示すよ うな多層配線基板を作った。

この時点で基板 1,1・・・内部 で互いに導通する導体 2.2・・・ の抵抗値を.最上段の基板の表 面に露出した導体表面 2a,2b 間 において測定しておく。

次ぎに上記実施例で得られた 導電ペーストを使用し,最も外 側の基板 1 の表面に露出した導 体表面を覆うよう同ペーストを スクリーン印刷し,これを空気 中において 850℃の温度を 10 分間与えて焼成して導体 3.3 を 設けた。なお、この際、基板の端部 に 1mm 角の引き出し電極部 5 を設けた。

3,3 間に互って RuO2 を主成分

[Example of usage, and EXPERIMENT]

Next, the electroconductive paste obtained in the above Example was used by the method like the next, and the test was performed.

The through-hole was filled with the above electroconductive paste while the screen printing of the electroconductive paste which essentially consists of Ni is carried out on the non-sintered ceramic sheet of thickness 200 micro-m which has some through-holes according to a predetermined wiring pattern.

Subsequently, this non-sintered ceramic sheet is heated for 10 minutes at the temperature of 125 degrees C. After drying, 4 sheets were laminated in the predetermined order and it was stuck by pressure.

Subsequently this is heat-treated at the temperature of 900 degrees C. After removing a ceramic sheet and the binder component in an electroconductive paste, it puts for 2 hours at the temperature of 1200 degrees C in N2 gas atmosphere containing 2% of H2. The multilayer wiring board which is shown in the drawing was made.

At this time, the resistance value of a conductors 2 and 2*** which conduct mutually within substrate 1,1***, is measured between conductor surfaces 2a and 2b which were exposed to the surface of the substrate of the

Next the electroconductive paste obtained in the above Example is used. The screen printing of said paste is carried out so that the conductor surface exposed to the surface of the most outer substrate 1 may be covered. In air, the temperature of 850 degrees C is provided for 10 minutes, and this is baked. Conductors 3 and 3 were provided.

In: addition, the lead-out electrode part 5 of 1 mm square was provided to the terminal part of a substrate at this time.

次いで新たに設けられた導体 Subsequently the resistive paste essentially consists of RuO2 is printed between とする抵抗ペーストを印刷し、 これを空気中において 850℃の 温度を 10 分間与えて焼成し、基 板 1 の上に被膜抵抗 4 を作製し た。

そしてこの導体 3,3 と被膜抵抗 4 を作製する前後において、それぞれ上記導体 2,2・・・の抵抗値を,その上に新たに設けられた上記導体 3,3 の表面 3a,3b で測定した上記抵抗値との比は,何れも 1.00 であり,酸化雰囲気中で焼成しても抵抗値の増化はみられなかった。これを別表の導通性の欄に「〇」で示した。

また、上記電極部 5 に 0.5 φの リード線6を半田付け7 し、同リード線6を基板1の表面に対し て垂直方向に引っ張って試験したところ、別表に示す通り、同電 極部5が基板1表面から剥離するときの引張強度は、何れも 1.0kg/mm2以上であった。

【比較例】

上記実施例に対して比較のため,別表の試料番号1,2,6,10~12,18~20,23,27,28,34,35,40~42,46~48,51,53,62,53,72及び78の各欄に示すように,この発明による導電ペーの組入を含むが,その試料を上記要件を満たさない試料を上記要件を満たして作り、この結果,別表被膜に示す側との結果,別表被膜に示す側が後に導体表面3a,3b間でそれぞれ測定した抵抗値と

the conductors 3 and 3 provided newly. In air, the temperature of 850 degrees C is provided for 10 minutes, and this is baked. The film resistance 4 was produced on the substrate 1.

And before and after producing these conductors 3 and 3 and the film resistance 4, the resistance value of above conductors 2 and 2 *** is respectively measured on the surfaces 3a and 3b of the above conductors 3 and 3 which were able to be newly provided on it. The ratio with the above resistance value which measured this on the conductor surfaces 2a and 2b is 1.00. Even when it baked in the oxidizing atmosphere, the gain of resistance value was not seen.

"(circle-symbol)" showed this to the column of the conduction property of an attached table.

Moreover, the lead wire 6 of 0.5 (phi) is soldered to the above electrode part 5. When said lead wire 6 was pulled perpendicularly to the surface of a substrate 1, and tested, the tensile strength in exfoliating said electrode part 5 from the substrate 1 surface was 1.0kg /mm2 or more as shown in an attached table.

[Comparative Example]

For the sake of a comparison with an above Example, as shown in each column of the sample numbers 1, 2, 6 10 - 12, 18 - 20, 23, 27, 28, 34 and 35, 40 - 42, 46 - 48, and 51, 53, 62, 53, 72 and 78 of an attached table, the same component as the electroconductive paste by this invention is contained. However, the composition ratio makes the specimen which does not fulfill the requirements for above, like an above Example. This was used on the same conditions as the example of above usage and EXPERIMENT, and this was tested.

As this result, as shown in each column of an attached table, the ratio of the resistance value respectively measured between conductor surfaces 3a and 3b before and after production of conductors 3 and 3 and the film resistance 4,

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導体表面 2a,2b 間で測定した抵抗値の比が 1.00 を越えるか(この抵抗値の比が 1.00 を越えるものを別表の導通性の欄に「×」で示した),または引張強度が1.0kg/mm2 未満であった。

and the resistance value measured between conductor surfaces 2a and 2b exceeds 1.00 ("*" showed that by which the ratio of this resistance value exceeds 1.00 in the column of the conduction property of an attached table.) Or tensile strengths was 1.0kg / mm2 or less.

【発明の効果】

【4.図面の簡単な説明】

図面は,この発明による導電ペーストの使用例を示す多層配線 磁器基板の厚さ方向の寸法を拡大した概略縦断面図である。 特許出願人 太陽誘電株式会社 代理人 弁理士 北條和由 別表

* は比較例として作製された 試料を示す

試料番号 組成比(重量%) 導通性 引張強度 kg/mm2

硝子

[EFFECT OF THE INVENTION]

As having explained above, according to this invention, a direct electroconductive paste is printed so that the above conductor surface may be covered, without carrying out a special anti-oxidation process of giving noble metals plating to the surface of a base metal conductor. And only by baking this in air, the conduction property required to compose an electric circuit, without oxidizing the conductor surface can be obtained.

For this reason, the number of processes reduction for producing circuit apparatuses, such as a hybrid integrated circuit, can be aimed at now.

[4. Brief Description of Drawings]

A drawing is the schematic cross-sectional chart to which the dimension of the thickness direction of the multilayer interconnection ceramic substrate which shows the example of usage of the electroconductive paste by this invention was enlarged.

PATENTEE Taiyo Yuden Co., Ltd. K.K.
Representative Patent attorney Kazuyoshi
Hojo
Attached table

* shows the specimen produced as Comparative Example.

Attached table

Row (left to right): Sample number, Composition ratio (weight%) (glass), Conduction property, Tensile strength kg/mm2

* shows the specimen produced as Comparative Example.

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*は比較例として作製された試 Row (left to right)

料を示す 試料番号

組成比(重量%)

導通性

Row (left to right) : Sample number, Composition ratio (weight%) (glass), Conduction property

引張強度 kg/mm2

硝子

*は比較例として作製された試

料を示す 試料番号

組成比(重量%)

Tensile strength kg/mm2

* shows the specimen produced as Comparative Example.

Row (left to right) : Sample number,

Composition ratio (weight%) (glass),

導通性

引張強度 kg/mm2

硝子

*は比較例として作製された試

料を示す 試料番号 Conduction property, Tensile strength kg/mm2

* shows the specimen produced as Comparative Example.

Row (left to right): Sample number,

組成比(重量%)

導通性

引張強度 kg/mm2

硝子.

(図示しない)

Composition ratio (weight%) (glass), Conduction property, Tensile strength kg/mm2

(No drawing)

手続補正書

昭和59年10月9日

特許庁長官 志賀 学殿

1.事件の表示

昭和 59 年特許願第 187067 号

Amendment

October 9th, Showa 59

Director-General of the Patent Office Mr.

Manabu Shiga

1. Display of an incident

Patent application of No. Showa 59 187067

【2.発明の名称】

厚膜用導電ペースト

3.補正をする者

2番12号

事件との関係 特許出願人

住所 東京都台東区上野 1丁目

氏名(名称) 太陽誘電株式会社

4.代理人 住所 310 茨城県水戸市五軒 [2. TITLE]

The electroconductive paste for thick films

3. Person Who Corrects

Relationship with the Incident PATENTEE

Address

Name Taiyo Yuden Co., Ltd. K.K.

4. Representative

Address

Name (8192) patent attorney Kazuyoshi Hojo

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(C) DERWENT

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氏名(8192)弁理士 北條和由 5.補正命令の日付 (自発)

6.補正により増加する発明の数 7.補正の対象 明細書の発明の詳細な説明の欄 8.補正の内容 別紙の通り

補正の内容

(1) 明細書第 2 頁上から 4 行~ 上から 11 行の文章を次ぎの通 り補正します。

5. Date of Correction Instruction (Spontaneity)

6. Number of Invention Increased by Correction7. Objective of correction

The column of the DETAILED DESCRIPTION OF INVENTION of Specification

8. Content of Correction The attached sheet

Content of a correction

(1) the sentences of 4th line of 2 page of specification from 11th line is corrected as follows.

"When baking electroconductive paste in air, in order to prevent the gain of the resistance value by the oxidation of a metal component, the electroconductive paste which essentially consists of noble metals, such as Ag, Au, and Pt, is used. However, these are expensive. Then the electroconductive paste which essentially consists of base metal, such as Ni, is used as an object for inexpensive. The method of baking this in inert gases, such as N2 gas, is utilised."

(2) "increasing" the 5th line from the bottom of the 8th page of Specification, is corrected to "an increase".



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